

Thickness-Dependence of the Coercive Field in Ferroelectrics

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Abstract

For forty years researchers on ferroelectric switching have used the Kay-Dunn theory to model the thickness-dependence of the coercive field; it works surprisingly well, despite the fact that it is based upon homogeneous nucleation and a small-field expansion, neither of which is realized in thin films. Here we demonstrate that this result can be obtained from a more general Kolmogorov-Avrami model of (inhomogeneous) nucleation and growth. By including a correction to the switching field across the dielectric that includes Thomas-Fermi screening in the metal electrode, we show that our theory quantitatively describes the coercive fields versus thickness in several different families of ferroelectric (lead zirconate-titanate [PZT], potassium nitrate, and polyvinylidenefluoride [PVDF]) over a wide range of thickness (5 decades). This agreement is particularly satisfying in the case of PVDF, as it indicates that the switching kinetics are domain-wall limited down to 1 nanometer and thus require no new effects.

Demand for integrated microelectronics with increased densities and decreasing voltage standards requires detailed characterization of the coercive field, E_c , for the design and fabrication of competitive, reliable ferroelectric devices. More specifically, recent measurements on nanometer ferroelectric films¹ have revealed a weakness in our current understanding of the thickness-dependence of E_c . Motivated by these experiments, in this Letter we present a new treatment of the coercive field as a function of thickness, $E_c(d)$, that incorporates both inhomogeneous nucleation in a finite-size film and field penetration in the electrodes. The $E_c(d)$ that emerges from our approach is in good agreement with observed behavior for films that range from 100 microns to 1 nanometer. Furthermore our approach indicates that the minimum film thickness, determined by the magnitude of the depolarization field,² can be tuned by varying the spontaneous polarization of the ferroelectric and the screening length of the electrodes. Other implications of our results for the processing windows of next-generation FeRAMS and DRAMS are also discussed.

For the last forty years the Kay-Dunn scaling law³ has been successfully used to describe the thickness-dependence of the coercive field in ferroelectric films ranging from 100 microns to 200 nanometers.⁴ However the Kay-Dunn model is based on assumptions, particularly that of homogeneous nucleation, which are inappropriate for thin films. As discussed in the original Kay-Dunn paper,³ the calculated energy barrier associated with such nucleation is several orders of magnitude larger than any experimentally determined value; furthermore the presence of long-range elastic interactions increases this barrier still further.⁵ Imaging measurements confirm the site-specific nature of nucleation in thin ferroelectric films, indicating that new domains nucleate at electrodes and at twin boundaries.⁶⁻⁹ The good agreement between measured values and the Kay-Dunn treatment of $E_c(d)$ is thus quite fortuitous.

Here we show that the Kay-Dunn scaling result can be recovered from an adapted Kolmogorov-Avrami model¹⁰ of inhomogeneous nucleation in a confined geometry. In this approach the transformation of a sample from paraelectric to ferroelectric is treated by considering the nucleation and growth of a single domain. The coercive field is determined by

the condition that

$$P(E, f) \Big|_{E=E_c} = \frac{1}{2} \quad (1)$$

where $P(E, f)$ is the untransformed sample fraction as a function of applied field E and frequency f . For inhomogeneous nucleation $P(E, f) \sim \exp -N(E)(v(E)\frac{2\pi}{f})^D$ where $N(E)$ and $v(E)$ are the field-dependent number of nucleation sites per unit area and domain growth velocity respectively and D is the dimension of the nucleus. The factor $(v(E)\frac{2\pi}{f})^D$ enters the formula for $P(E, f)$ as the characteristic volume of a growing nucleus over the cycle time of the electric field. However if the nuclei elongate through the thickness of the film before colliding with another domain, this factor should be replaced by (κd) where κ is the (small) transverse area of the needle-shaped domain and d is the film thickness. Such a morphology is supported by experimental observation.¹¹ Then we obtain $P(E) \sim \exp -N(E)(\kappa d)$ where $N \sim E^\alpha$. α is known to equal 3/2 over a fairly broad range of fields both experimentally¹² and theoretically¹³ from switching kinetics; this then leads to the desired result, $E_c \sim d^{-2/3}$. Here $0 < \kappa < 1$ indicates the size of the nucleating grain as a fraction of the film thickness. We note that the scaling of E_c with thickness follows directly from the field-dependence of the number of nucleation sites per unit area, $N(E)$; this result could be checked independently by tuning $N(E)$ and observing the predicted change in $E_c(d)$.

Recently it has been possible to measure the coercive field of ferroelectric PVDF films with thicknesses less than 100 nanometers; on these length-scales significant deviation from the scaling (cf. Figure 1) described above is observed.¹ In retrospect, there were already hints of this new behavior in $E_c(d)$ for films between 100 and 200 nanometers,¹⁴ but the recent measurements down to 1 nanometer are quite conclusive.¹ The scaling treatment of $E_c(d)$ assumes perfect conducting plates, and here we have modified it to include field-penetration in the electrodes. We show that the latter effect becomes important for small film thicknesses and is responsible for the observed deviation from the expected scaling behavior (cf. Figure 1). Furthermore we demonstrate that, using these ideas, we can include a correction to the measured coercive fields and recover the scaling result for films ranging

from 100 microns down to 1 nanometer (cf. Figure 2).

In an idealized ferroelectric capacitor, the plates are assumed to be perfect conductors and charge resides on a plane of negligible thickness at the electrode-ferroelectric interface, compensating for the spontaneous polarization in the ferroelectric film. Realistically this charge distributed over a small but finite length-scale in the metal, λ . The resulting electric field leads to an associated voltage drop in the metal electrodes. A compensating depolarization potential, Φ_{dp} , must exist across the film to ensure that it is an equipotential in the absence of an externally applied voltage. The associated field, $E_{dp} = \frac{\Phi_{dp}}{d}$, assists in the switching process so that the measured coercive field, E_c^{meas} , is

$$E_c^{meas} = E_c^i - E_{dp} \quad (2)$$

where E_c^i refers to a perfect capacitor with negligible screening and is described by the Kay-Dunn scaling.

In order to determine Φ_{dp} , and its associated field, we assume that the charge density takes the form

$$\rho(x) = \frac{Q}{\lambda} e\left(-\frac{x}{\lambda}\right) \quad (3)$$

and, furthermore we assume symmetric capacitor plates; then, using the fact that the potential in the electrodes is related to the induced charge density, we find

$$|\Phi_{dp}| = \left| \left(\frac{4\pi}{\epsilon_m} \right) \frac{2\lambda Q d}{A} \right| \quad (4)$$

where ϵ_m refers to the metallic dielectric constant, and $Q = \frac{P_s A}{d}$ in a ferroelectric where P_s is the spontaneous polarization. Here we estimate λ using the assumption of a slowly varying potential,²⁰ resulting in $\lambda^2 = \epsilon_m \lambda_{TF}^2$ where λ_{TF} is the Thomas-Fermi screening length. Experimentally P_s is observed to be independent of film thickness in the nanometer PVDF samples studied¹, indicating that Φ_{dp} is a constant; note that in this case the voltage drop across the electrodes, $V_{electrodes}$, compensates for the depolarization potential Φ_{dp} . However E_{dp} scales inversely with d , so that it assumes increasing importance in the expression for E_c^{meas} , (2), with decreasing film thickness.

Field-penetration of the electrodes has been studied in the context of very thin (~ 30 angstroms) film capacitors by several authors,^{15–18} and here we argue that it is relevant for thicker films whose dielectric constant, ϵ_f is large. The effective capacitance of the metal-film-metal sandwich can be determined by contributions from two capacitors in series¹⁶

$$\frac{1}{C} = \frac{1}{C_{film}} + \frac{1}{C_{electrodes}} \quad (5)$$

where C_{film} and $C_{electrodes}$ are the film and the electrode capacitances respectively; the first term is geometric and the second provides an upper bound to the capacitance with decreasing film thickness. For a dielectric film, the voltage drop is $V_{film} = \frac{4\pi}{\epsilon_f} \left(\frac{Qd}{A} \right) d$, so that the fraction of the total potential difference, $V = V_{film} + V_{electrode}$, across the electrodes is

$$\frac{V_{electrodes}}{V} = \frac{2\lambda \left(\frac{\epsilon_f}{\epsilon_m} \right)}{d + 2\lambda \left(\frac{\epsilon_f}{\epsilon_m} \right)} \quad (6)$$

which can be substantial for large ϵ_f and small d . Therefore we note that field-penetration effects will be important for both (non-switching) high-dielectric DRAM capacitors and in switching FeRAMS.

Let us now turn to a more quantitative analysis. In Figure 1, we display the measured coercive field data¹ for PVDF and the Kay-Dunn scaling prediction. We note that there is deviation from the scaling behavior at approximately 100 nanometers. Next, using (2), we plot the coercive field including the effect of field-penetration. We have used the value of $\epsilon_f = 14$ for PVDF from experiment,¹⁹ and used $\epsilon_m = 1$ and $\lambda_{TF} = 0.45$ angstroms for the aluminum electrodes.²⁰ For thicknesses greater than 100 nm, the modified and the scaling curves are identical, indicating that the depolarization contribution is not important in this regime. However the modified E_c continues to display a good fit to the data for nanometer thicknesses, particularly as it deviates from the scaling curve. We note that the observed rollover in $E_c(d)$ will correspond to the thickness where the depolarization and the idealized coercive fields are comparable; here we expect a polarization instability² that will determine the minimum allowed film thickness, d_{min} . We note that our results suggest that this instability can be tuned by varying the spontaneous polarization of the ferroelectric

and the screening length of the electrodes. This is consistent with the results of Ghosez and Rabe²¹ who found that d_{min} for a ferroelectric film with perfect electrodes was less than that found with semiconducting ones.²

Alternatively we can use (2) to add depolarization corrections to the measured coercive field; the resulting idealized E_c^i displays Kay-Dunn scaling for five decades in thicknesses ranging from 100 microns to 1 nanometers (cf. Figure 2). We present the modified data for three different materials in the main part of the figure; since $E_c = C \times d^{-2/3}$ where C is material-specific, we expect universal behavior for $\log E_c - \log C$. Indeed this is the case, as indicated in the inset of Figure 2. It is unusual to see universal scaling over such a large number of decades. The agreement between theory and experiment is particularly satisfying for the case of PVDF, since it demonstrates that the switching kinetics of films on nanometer scales are domain-wall limited and are qualitatively similar to those of their 100 micron counterparts. No unusual effects special to ultrathin films are required; this has been a topic of discussion in the literature.²²

Our results have several implications for the design and fabrication of ferroelectric devices. Ideally FeRAMS should be designed at film thicknesses where the measured coercive field is less than the scaling value, but before it is equal to the depolarization field; this gives a processing window for PVDF, the polymeric ferroelectric used for this study, for 10 - 100 nm. Furthermore the minimum film thickness, associated with a polarization instability, can be tuned by varying P_s and λ . Oxide electrodes, known for reducing ferroelectric fatigue⁴, would *not* be optimal for very thin (< 10 nm) devices due to large field-penetration in the capacitor plates. Indeed the optimization of very thin devices should emphasize the screening properties of the electrodes, favoring Pt or Au over $SrTiO_3$. For the DRAM market, the primary objective is maximizing total capacitance; our results indicate that it is limited by the electrodes. Thus use of larger dielectric materials and thinner films will *not* improve it significantly. Instead one should optimize the electrical resistivity of the ferroelectric film and the screening properties of the electrodes.

In summary, in this Letter we have brought together the ideas of Kay and Dunn,³ Batra

and Silverman,² and Ghosez and Rabe²¹ to develop a model for the coercive field as a function of thickness. For thin films, we have shown the importance of field-penetration in the electrodes; the resulting depolarization field is a function of the spontaneous polarization of the ferroelectric and the Thomas-Fermi screening length of the metal electrode. Naturally when E_{dp} becomes equal to the idealized coercive field the polarization is unstable;² however when it is comparable but less than E_c^i , it contributes to the switching. In Figure 1, with no adjustable parameters, we display good agreement between our modified coercive field and that measured in PVDF, particularly for thicknesses < 100 nm where there is deviation from scaling behavior. In Figure 2 the measured data are corrected to accommodate field-penetration in the electrodes; the result obeys Kay-Dunn scaling for five decades in length-scale. Our results indicate that the choice of electrode is very important for optimizing performance for very thin film devices. Given increasing clock speeds, an improved understanding of the coercive fields at finite frequencies would also be of great interest for the development of future ferroelectric devices.

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Figure Captions

Fig. 1. Measured coercive field data¹ for PVDF, the Kay-Dunn scaling and the current theory vs. thickness; as explained in the text, the latter incorporates field-penetration effects via a depolarization contribution to the field as a function of thickness.

Fig. 2. (Main Figure) The corrected log coercive field vs. log thickness where the depolarization contribution has been subtracted from the measured data **(Inset)** Normalized corrected log coercive field vs. thickness which indicates Kay-Dunn scaling over five decades of lengths; here universal behavior is shown for $\log E_c - \log C$ where C is defined by the expression $E_c = C \times d^{-2/3}$ and is material- and sample-specific.

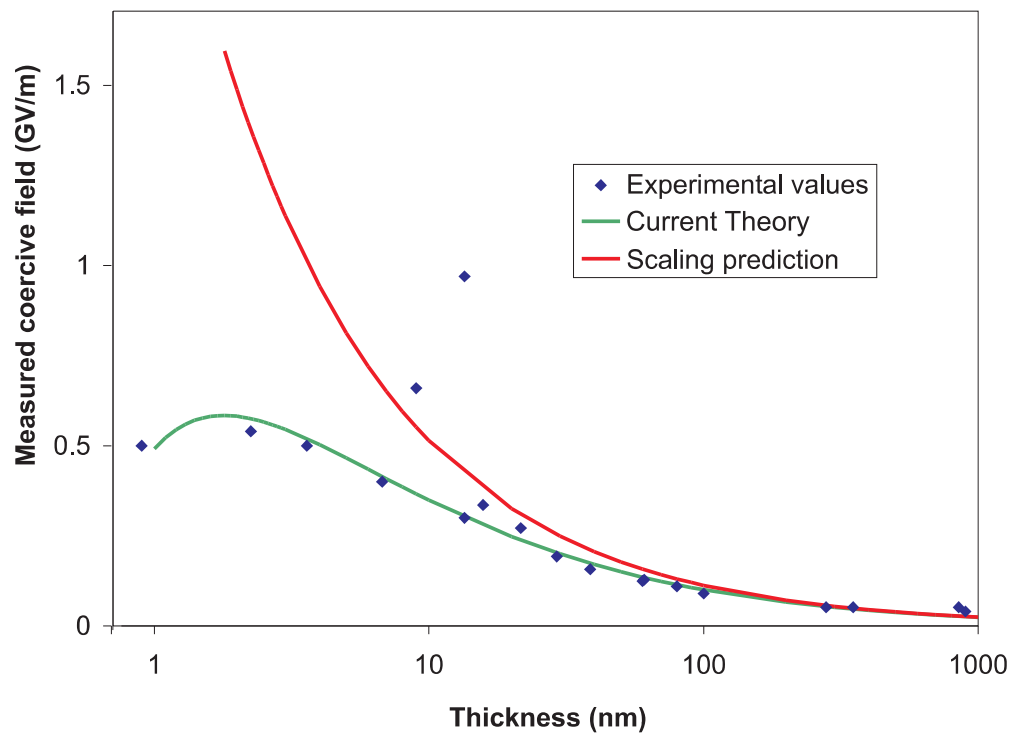


Fig. 1

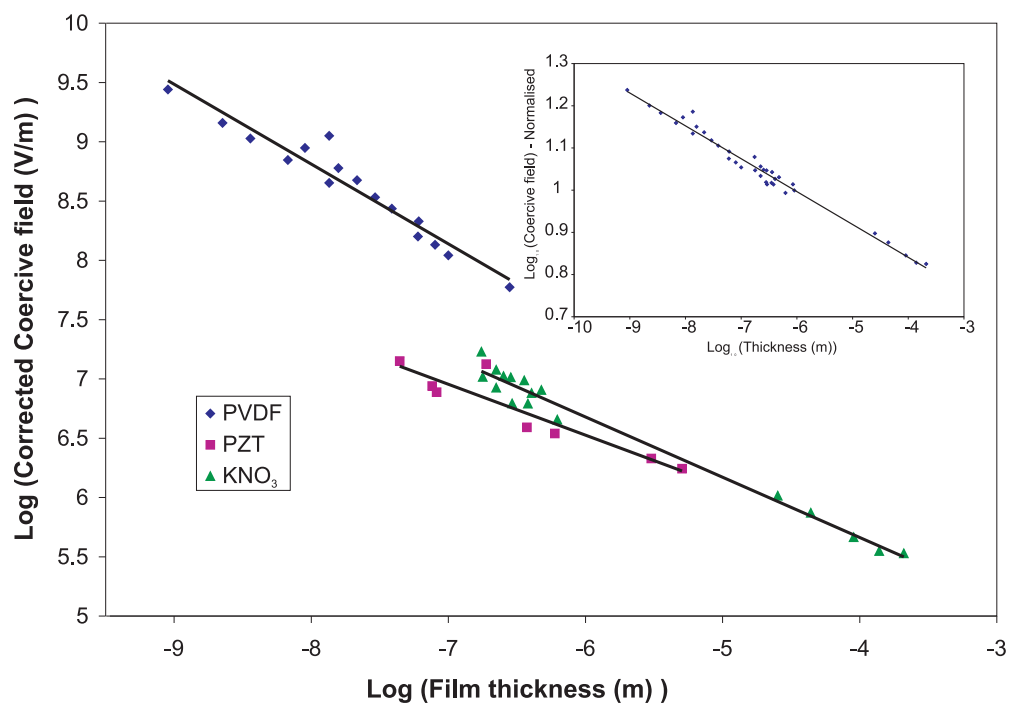


Fig. 2